NR Vulcanisates with Improved Dynamic Properties

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The hysteresial properties of rubber vulcanisates depend not only on the nature of the polymer, the nature and degree of cross-linking but also on the type, amount and degree of dispersion of the filler. This paper describes how Nitrol—a new Monsanto chemical promoter—may be employed to produce improved dispersion of carbon black in natural rubber and thus provide vulcanisates with higher resilience and lower heat build-up. Various Banbury mixing treatments are shown by sensitive dynamic test procedures to lead to reductions in both 'in-phase' and 'outof-phase' moduli, mechanical phase angle and improvements in black dispersion.

Vulcanised rubber is not perfectly elastic. Heat is generated when it is subjected to cyclic strains, as in a tyre. The quantity of heat generated per cycle by unit volume of rubber is approximately proportional to the product of the 'out-of-phase' or loss modulus of the rubber and the square of the strain amplitude. The strain amplitude can be kept low by suitable design but it is difficult to obtain a low loss modulus without reductions in other important properties. Chemical promoters have been developed (MONSANTO, 1967) to produce compounds with significantly reduced loss moduli, and, consequently, lower operating temperatures. This paper is concerned with a study of the dynamic properties of natural rubber tyretread formulations compounded with a promoter recently developed by Monsanto Chemical Co., Nitrol, which consists of $\frac{2}{3}$ inert clay diluent and $\frac{1}{3}$ of the active chemical. N-(2methyl-2-nitropropyl)-4-nitrosoaniline.



GESSLER (1953), showed that the hysteresis of carbon black-filled butyl rubber was greatly

reduced by heat treatment of the compound during mixing. Subsequently it was found that the effect of hot mixing could be greatly accelerated by the addition of para-dinitrosobenzene (GESSLER AND FORD, 1953) and other promoters (LEEPER et al., 1956; MONSANTO, 1967). BUCKLEY (1957) found greatly improved heat build-up and general durability of butyl tyres in high speed wheel tests under severe overload. PAYNE (1963) showed that heat treatment of butyl compounds using the promoter Elastopar produced profound changes in dynamic properties and much lower hysteresis. Other workers such as PAYNE (1965a and b), BOONSTRA and MEDALIA (1963), BOLT et al. (1960), DANNENBERG (1952) and DANNENBERG et al. (1961) have shown a clear dependence of dynamic properties such as 'in-phase 'and 'outof-phase' modulus and loss angle on carbon black dispersion, assessed by optical and electron microscopy and electrical conductivity. In particular, PAYNE (1965a) and BOONSTRA AND MEDALIA (1963) correlated the degree of dispersion with shear modulus changes on oscillation. In the present paper, this shear modulus change is referred to as $(G_{0}' - G_{00}')$ and is used as an index of carbon black dispersion. This is in preference to optical or electron microscopic counting methods, which are difficult to use in a quantitative manner in the well-dispersed systems studied by the authors.

EXPERIMENTAL	
The base formulation used was as	s follows:
Heveacrumb SMR 5	100
HAF black	50
Paraffinic oil (Petrofina 2069)	4.7
Stearic acid	2
Zinc oxide	5
Anti-oxidant (Nonox ZA)	2
Sulphur	2.5
CBS (Santocure)	0.5
Nitrol	as shown

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The base formulation was prepared in a first mixing stage in a laboratory BC Banbury, using the upside-down mixing cycle shown in *Table 1*.

Nitrol in various concentrations was usually

added in a second mixing cycle at a high temperature. Steam at 55-60 lb/in^2 was applied to the Banbury, the batch temperature being $180^{\circ}-185^{\circ}C$ after mixing times of five to ten minutes. *Table 1* gives details of mixing cycles employed for Compounds 1-8. Compounds 1, 2 and 3 were control compounds without Nitrol, of which Compound 3 received the second mixing stage, but Compounds 1 and 2 did not. The addition of Nitrol during the first stage, either with the black (Compound 8) or after dispersion of the black, was ineffective even after prolonged mixing.

Banbury temperature and power consumption were recorded throughout. The compounds were tested according to the appropriate

TABLE I. MIXING SCH	IEDULES AND	PROCESSING	PROPERTIES

Banbury procedure				Compo	und No.			
Danoury procedure	1	2	3	4	5	6	7	8
First stage (Banbury temperature 100°C - 140°C)								
0 min – Add black, zinc oxide, stearic acid, anti-oxidant, oil, SMR in this order								Add 0.6 Nitrol with black
3 min $-$ Dump and cool overnight								UIGUK
Dump temperature, °C	160	GT7TA	178	182	178	185	182	183
Mooney viscosity 100°C (MS3*)	60	56	54	92.54	52	49	52	53.5
Second stage (Banbury temperature 140°C)	9-1			IA				
0 min — Add masterbatch		、具		.				
🚦 min — Add Nitrol where shown	8-	LEIN		0.6	1.2	3.0	0.6	+ -
$5 \min - Dump$ and cool overnight	KAL.	No. of Concession, name	1	Sol				
Dump temperature, °C	-31	W-RU	183	183	197	193	206	200
Mooney viscosity 100°C (MS3)	-	-	34.5	63.5	147	239	54	34
Third stage Add S and CBS on mill								
Mooney viscosity 100°C (MS3)	41.5	38.5	28	38	62.5	118	35.5	26.5
Mooney viscosity 120°C (MS3)	36	34.5	24	31	47	99.5	29	24.5
Mooney scorch 120°C T5 min	16	15.3	15	11.5	9	4.2	8.5	15

*Small rotor used throughout

†Dumped at 10 min



Compound 3: (Table 1) Control, mixed for 5 min after ram down. **Compound 4:** 0.6 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $4\frac{1}{2}$ min. **Compound 5:** 1.2 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $4\frac{1}{2}$ min. **Compound 6:** 3.0 p.p.h.r. Nitrol added $\frac{1}{2}$ min. after ram down and mixed for further $4\frac{1}{2}$ min. **Compound 6:** 3.0 p.p.h.r. Nitrol added $\frac{1}{2}$ min. after ram down and mixed for further $4\frac{1}{2}$ min. **Compound 7:** 0.6 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $9\frac{1}{2}$ min. **Compound 7:** 0.6 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $9\frac{1}{2}$ min. **Compound 8:** 0.6 p.p.h.r. Nitrol added during the addition of black in the first stage and given a second stage.



Figure 2. Wattmeter plots obtained during second stage addition of Nitrol to gum compounds. A — Control mixed for 5 min after ram down. B — 0.6 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $4\frac{1}{2}$ min.

C = 1.2 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $4\frac{1}{2}$ min. D = 3.0 p.p.h.r. Nitrol added $\frac{1}{2}$ min after ram down and mixed for further $4\frac{1}{2}$ min. British Standards (SCOTT, 1965). In measuring Mooney viscosity, the small rotor was employed because of the high compound viscosity.

The dynamic experiments were performed on the variable amplitude dynamic tester described by PAYNE (1961, 1965c). The dynamic properties of a filler-loaded vulcanisate are very sensitive to strain history and the experimental procedure was first to take measurements at the lowest strain possible and then to increase the strain by increments to the maximum capacity of the machine. At each strain, measurements of phase angle and the amplitudes of the oscillatory stress and strain were taken.

The ratio of the stress amplitude to the strain amplitude gave the complex shear modulus G^* where

$$G^* = G' + iG''$$

or $G^* = (G'^2 + G''^2)^{\frac{1}{4}}$

G' and G'' being the 'in-phase' and 'out-of-phase' components of the complex shear modulus respectively. Phase angle δ is related to G' and G'' by

$$\tan \delta = G''/G'$$

The dynamic parameters have been fully discussed in earlier publications (PAYNE, 1965c).

EFFECT OF NITROL ON THE UNVULCANISED COMPOUND

Increasing proportions of Nitrol progressively increase compound viscosity during mixing. *Figure 1*, plotting power consumption against mixing time, shows that the normal breakdown in viscosity during the second stage of mixing (Compound 3, no Nitrol) is inhibited by 0.6 p.p.h.r. of Nitrol (Compound 4). Compounds 5 and 6 with 1.2 p.p.h.r. and 3.0 p.p.h.r. of Nitrol show a pronounced increase in viscosity during mixing. More prolonged mixing of a compound with 0.6 p.p.h.r. of Nitrol (Compound 7) again reduces the compound viscosity. Adding Nitrol in the first mixing stage is ineffective (Compound 8).

Adding Nitrol to an unfilled compound also increases power consumption (*Figure 2*) and it may be tentatively suggested that the increase in viscosity (*Table 2*) is a contributing factor towards better dispersion of the filler and hence

TABLE 2.EFFECT OF NITROL ONVISCOSITY OF GUM COMPOUNDS

		(· · ·		
Nitrol, p.p.h.r.	0	0.6	1.2	3.0
Mooney viscosity (MS 3)		l T	. 	
After second stage	19	61	76	83
After third stage	18.5	18.5	56	*
	1			l

Base compound: SMR 5L, 100; zinc oxide, 5; stearic acid, 2; Nonox WSP, 1; sulphur, 2.5; CBS, 0.5; Nitrol, variable.

*Too scorched to handle

the superior dynamic properties to be discussed later.

The large viscosity increases due to Nitrol and the reduction in viscosity on further working are also shown in *Figure 3*, where the reading of a Mooney viscometer is plotted against time in the viscometer for compounds as dumped from the Banbury after the second mixing stage. *Figure 4* shows similar data for compounds after the addition of sulphur and CBS on a mill (4 min at 70°C) showing that the large viscosity increases due to Nitrol treatment are reduced by working on the mill, but are still significant. Part of the viscosity breakdown due to working is recoverable in a compound treated with Nitrol, but not in an untreated compound (*Figure 5*).

However, as *Figure 4* shows, the two control compounds (1 and 2), which were not given a second mixing stage and were therefore less broken down, had a viscosity higher than that of a compound treated with 0.6 p.p.h.r. of Nitrol and equal to that of a compound treated with 1.2 p.p.h.r. of Nitrol.

Increasing proportions of Nitrol give marked decreases in scorch resistance (Table 1). In view of this, and the increased viscosity and power consumption noted above, the use of no more than 0.6 p.p.h.r. of Nitrol is considered satisfactory (MONSANTO, 1967). As will be seen later, this proportion of Nitrol is sufficient to impart marked changes in dynamic properties.

EFFECT OF NITROL ON GENERAL VULCANISATE PROPERTIES

Comparing compounds with similar mixing history (*Table 3*, Compounds 3, 4 and 5) the use of 0.6 p.p.h.r. of Nitrol in a HAF black-filled compound increases Lüpke resilience by 3.5%.



Figure 3. The change in Mooney viscometer reading with time in the viscometer for untreated and Nitrol-treated compounds as taken from the Banbury after the second stage of mixing.

TABLE 3.	EFFE	CT OF	NITROL O	N
RESILIENCE	AND	HEAT	BUILD-UP	OF
HAF E	BLACK	COM	POUNDS	

Properties	Compound No.				
	3	4	5		
Nitrol, p.p.h.r.	0	0.6	1.2		
Lüpke resilience 21°C, %	68,5	72	72		
Goodrich flexometer heat build-up, °C	35.4	32.2	33.3		

with a corresponding decrease in heat build-up; 1.2 p.p.h.r. of Nitrol gives no further improvement. Similar effects are obtained (*Table 4*) with other carbon blacks.

The effect of Nitrol treatment on modulus properties (*Table 5*) is that hardness is reduced, modulus at 100% extension is unchanged, and modulus at 300% extension is increased. Similar effects have been found previously with heat treatment, particularly of butyl rubber, and correlate with improved dispersion of carbon black. There is a progressive decrease in elongation at break with increasing Nitrol



Figure 4. The change in Mooney viscometer reading with time in the viscometer for untreated and treated compounds after the addition of sulphur and CBS on the mill. Compounds 1 and 2 did not receive a second mixing stage in the Banbury.

TABLE 4.	EFFECT OF	NITROL ON
RESILIENCE	AND HEAT	BUILD-UP OF
COMPOUNDS (CONTAINING	OTHER BLACKS

Compounds	Lüpke re 21°	esilience, C, %	Goodrie meter build-	rich flexo- ter heat d-up, °C	
Nitrol, p.p.h.r.	0 0.6		0	0.6	
ISAF	64.0	68.5	43.7	39.4	
SAF	59.0	63.5	45.5	41.0	
Regal 300	67.5	72.5	36.6	33.8	
Vulcan 6H	62.0	64.5	43.6	43.1	
United SPF	65.0	70.0	41.4	38.6	

content but tensile strength is unaffected by 0.6 p.p.h.r. of Nitrol. There is a small improvement in laboratory abrasion resistance, flexcracking resistance and permanent set in the Goodrich flexometer heat build-up test. There is a decline in cut growth resistance and in tear resistance at 21°C and 100°C.

The Nitrol-treated Compound 4 can also be compared (*Table 6*) with Compound 1, which did not receive the second hot-mixing stage and is the compound which would normally be prepared by the usual mixing techniques. This is therefore a better technological assessment of the effects of Nitrol treatment. Comparing Compounds 1 and 4 (*Table 6*), the improvements in resilience and heat build-up on Nitrol treatment, though still present, are less than



Figure 5. Recovery of viscosity on standing after working. Dots show the change in Mooney viscometer reading with time in the viscometer for untreated and treated compounds. Open circles show similar data for the same samples after overnight recovery.

Properties	Com	pound	No.
	3	4	.5
Nitrol, p.p.h.r.	0	0.6	1.2
Hardness, IRHD	61	60	59.5
M100, kg/cm ²	23	24	23
M300, kg/cm ²	130	151	154
Tensile strength, kg/cm ²	256	261	243
Elongation at break, %	485	455	415
Laboratory Akron abrasion loss, ml/500 rev	0.033	0.031	0.030
De Mattia flex-cracking resistance, kc to grade C	175	207	293
Permanent set after Goodrich flexometer test, %	3.2	2.8	2,8
De Mattia cut-growth resistance kc from 4–8 mm	78	56	22
Fear resistance, split strip method, kg/mm			
at 21°C	1.82	1.22	1.03
at 100°C	2.49	2.05	1,54
at 140°C	1.62	1.65	1.71

TABLE 5. EFFECT OF NITROL ON SOME VULCANISATE PROPERTIES

those noted in comparing Compounds 3 and 4. Abrasion resistance is unchanged, flex-cracking resistance is improved, and tensile strength, elongation at break, tear strength and cutgrowth resistance are reduced. Modulus and hardness changes are similar to those previously indicated.

EFFECT OF NITROL ON DYNAMIC PROPERTIES

The variation of 'in-phase' shear modulus (G') against double strain amplitude* of oscillation is shown in *Figure 6* for the mixes 1-8 described in *Table 1*. The typical sigmoidal change of

modulus with amplitude is apparent in all the vulcanisates. It has been shown earlier (PAYNE, 1965c) that the 'in-phase' shear modulus has one limit at low strains (G'_o) and a further limit (G'_{oo}) at high strains. The difference between the two limits $(G'_o - G'_{oo})$, the shear modulus change with amplitude, has been shown previously (PAYNE, 1965a and b, BOONSTRA AND MEDALIA, 1963) to decrease with improvement in dispersion as reflected by electron microscope studies or by conductivity measurements on the filler-loaded vulcanisates.

Figure 6 shows that, as a group, Compounds 4, 5, 6 and 7 (all containing Nitrol added in the second stage) have much lower 'in-phase' shear moduli than the group of untreated Control Compounds 1, 2 and 3. Nitrol-treated vulcani-

TABLE 6. COMPARISON OF NITROL TREATMENT WITH SINGLE STAGE MIXING

Properties	Compo	und No.
	0	4
Nitrol, p.p.h.r.	0	0.6
Mooney viscosity 100°C (MS3)	41,5	38.0
Tensile strength, kg/cm ²	281	261
Elongation at break, %	515	455
M100, kg/cm ²	23	24
M300, kg/cm ²	129	151
Hardness, IRHD	62.5	60.0
Lüpke resilience, 21°C, %	70.0	72.0
Lüpke resilience, 100°C, %	77.0	79.5
Goodrich flexometer heat build-up, °C	33.3	32.2
Laboratory abrasion resistance (Akron vol. loss, ml/500 rev)	0.030	0.031
De Mattia flex-cracking resistance, kc to grade C	119	207
De Mattia cut-growth resistance kc from 4-8 mm	74	56
Tear strength, 21°C, kg/mm	2.9	1.2

^{*}The double strain amplitude is twice the deformation imposed in sinusoidal strain.



Figure 6. Variation of 'in-phase' shear modulus G' with double strain amplitude for Compounds 1–8.

sates thus offer less resistance to small shear forces and it is understandable that they exhibit less heat build-up.

Figure 6 and data derived from it in Table 7 show that the modulus changes observed in the Nitrol-treated Compounds 4, 5, 6 and 7 are substantially lower than those observed in the control Compounds 1, 2 and 3. This indicates the better dispersion of the Nitrol-treated compounds compared with untreated compounds. Compound 7 (given a prolonged 10-minute second stage treatment with Nitrol) exhibited the lowest G'_o value and the lowest $(G'_o - G'_{oo})$ value and was the best dispersed mix. Addition of Nitrol with the black in the first stage followed by a second stage (Compound 8) is relatively ineffective and gives intermediate G'_o and $(G' - G'_{oo})$ values. Other treatments in which Nitrol was added during a prolonged first stage process were shown to be ineffective and data on these are therefore not presented here.

The variation of phase angle (δ) with double strain amplitude of dynamic oscillation is shown in *Figure 7* for selected compounds. Values of the maximum phase angle (δ_{max}) for all the compounds are listed in *Table 8*, the values of δ_{max} for Nitrol-treated Compounds 4-7 being approximately 1 degree or 20% less than the δ_{max} values of Compounds 1-3. The variation of the 'out-of-phase' shear modulus (G'') with double strain amplitude is given in *Figure 8*. Values of the loss modulus G''_{max} for



Figure 7. Variation of phase angle (δ) with double strain amplitude for Compounds 1, 2, 5 and 7.

-	<i>C</i> (Cr 10-2	G'a - G'aa	G"mar		Lüpke res	silience, %	Goodrich	Dunlop resilience
Com- pound	dyne/cm ²	dyne/cm ²	$\times 10^{-7}$ dyne/cm ²	× 10 ⁻⁶ dyne/cm ²	(degrees)	21°C	100°C	heatbuild- up, °C	21°C on Goodrich flexometer sample
1	1.47	0.80	0.67	1.13	5.9	70.0	77.0	33.3	74.0
2	1.49	0.81	0.68	1 .29	6.6	68.0	77.5	35.0	72.8
3	1.38	0.76	0.62	1.05	5.8	68.5	81.0	35.4	73.5
4	1.05	0.76	0.29	0.80	4.9	72.0	79.5	32.2	77.0
5	1.01	0.76	0.25	0.72	4.8	72.0	79.5	33.3	77.5
6	1.05	0.79	0.26	0.83	5.4	69.0	79.5	34.6	76.0
7	0.98	0.77	0.21	0.69	4.7	69.0	81.5	34.7	76.5
8	1.22	0.79	0.43	0.95	5.8	70.0	79.0	34.9	74.8

 TABLE 7. CORRESPONDENCE OF LIMITING DYNAMIC PARAMETERS WITH PHYSICAL TESTING DATA



Figure 8. Variation of 'out-of-phase' shear modulus (G'') with double strain amplitude for Compounds 1–8.

Compounds 4-7 are approximately 40% lower than the values for Compounds 1-3. Values of G^*_{max} for the eight vulcanisates correlate with the resilience and heat build-up data given in *Table 7*.

 G''_{max} has been plotted against $(G' G'_{00})$ in Figure 9 for the eight vulcanisates studied. A linear relationship obtained can be expressed as:

 $G''_{max} = 0.53 \times 10^6 + 0.095 (G'_o - G'_{oo})$

This relationship is similar to the one obtained earlier (PAYNE, 1965c). The intercept at $(G'_{0} - G'_{00}) = 0$ is assumed to be the 'out-of-phase' shear modulus of an ideally dispersed vulcanisate.

The results of the measurements in *Table* 7 enable the different mixing treatments to be ranked according to their effectiveness in producing a good dispersion of black. The ranking order in improving quality is:

- A 3-minute first stage Banbury mixing cycle beginning at 140°C and dumping at 177°C;
- 2. A 3-minute first stage mixing cycle beginning at 100°C and dumping at 160°C;

- 3. An additional 5-minute second stage treatment;
- 4. A 5-minute second stage treatment with 0.6 p.p.h.r. Nitrol;
- 5. A 5-minute second stage treatment with 1.2 p.p.h.r. Nitrol; and
- 6. A 10-minute second stage treatment with 0.6 p.p.h.r. Nitrol.

EFFECT OF CARBON BLACK LEVEL IN NITROL-TREATED COMPOUNDS

For some purposes, *i.e.*, to meet the requirement of a particular application or a specification, it is necessary to maintain a given value of a property such as hardness. It may therefore be necessary to change the black level in order to maintain a given property constant after Nitrol treatment, and the effect of this is shown in *Table 8*. In changing from 40 to 60 p.p.h.r. of HAF black, the hardness increases 7.5

IRHD and Lüpke resilience is reduced from 72.5 to 69.5% at 21° C and from 83 to 77% at 100°C. If one has to compensate for a loss of hardness of 2 IRHD, an extra 5 p.p.h.r. black are necessary and the loss of resilience may be expected to be 0.75% at 21° C and 1.5% at 100°C. The resilience loss due to an increase in black level is less than that gained by Nitrol treatment and the overall advantage due to Nitrol is confirmed.

To meet specifications involving modulus at high extensions, it might be desirable to use less carbon black in conjunction with Nitrol treatment, and in this case, hysteresis is further reduced.

The dynamic properties of Nitrol-treated compounds containing varying amounts of HAF black are shown in *Figure 10*. At 50 p.p.h.r. of HAF black there are the reductions in shear modulus G' and in shear modulus



Figure 9. Variation of G^{max} with (G'o-G'oo) for Compounds 1-8.

Properties	HAF black, p.p.h.r.						
	40	45	50	55	60		
Nitrol, p.p.h.r.	0.6	0.6	0.6	0.6	0.6		
Mooney viscosity 100°C (MS 3)	20	22	24	25.5	29		
Tensile strength, kg/cm ²	308	298	280	273	257		
Elongation at break, %	535	490	450	430	415		
100% modulus, kg/cm²	20	23	26	29	29		
300% modulus, kg/cm ²	130	150	167	180	178		
Lüpke resilience 21°C, %	72.5	71.0	72.0	70.0	69.5		
Lüpke resilience 100°C, %	83,0	82.0	80.5	79.0	77.0		
Goodrich flexometer heat build-up, °C	27.3	31.3	34.2	38.5	42.4		
Laboratory abrasion resistance (Akron vol. loss, ml/500 rev)	0.025	0.027	0.021	0.026	0.024		
Hardness, IRHD	59,0	61.5	63.5	66.0	66.5		

TABLE 8. EFFECT OF BLACK LEVEL ON PROPERTIES OF NITROL-TREATED COMPOUNDS

Mixing was carried out as indicated for Compound 4, Table 1.

change $(G'_o - G'_{oo})$ already noted. Increasing the black content of the Nitrol-treated compound to maintain parity of hardness with the untreated compound increases the shear modulus change $(G'_o - G'_{oo})$, *i.e.*, it tends to bring the treated compound back towards its untreated control. Reducing the black content to maintain, for example, parity of M300 modulus, further diminishes the shear modulus change. In unfilled compounds, treated or untreated, the shear modulus change is almost zero.

CONCLUSIONS

The effect of Nitrol on a natural rubber tyretread compound is to increase its viscosity while it is in the Banbury mixer. Vulcanisates prepared from compounds treated with 0.6 p.p.h.r. Nitrol in an additional second stage process have superior resilience and reduced heat build-up compared with untreated control compounds. Laboratory abrasion resistance is maintained or improved and De Mattia flexcracking resistance is enhanced by Nitrol but tensile strength, tear strength, cut growth resistance and elongation at break are reduced. The hardness of Nitrol-treated compounds is reduced, modulus at 100% extension is relatively unchanged but modulus at 300% extension is increased consistent with improvements in dispersion of the black filler.

Dynamic testing has shown with much greater sensitivity than would be possible with conventional testing that treatment with Nitrol reduces hysteresial losses. Reductions in hysteresis occur in the strain amplitude region important in the working of a tyre and the operation of rubber products in engineering applications.

Improved resilience of natural rubber compounds is expected to be reflected by an increase in the life of products run under conditions close to blow-out, and should permit



Figure 10. Variations of 'in-phase' shear modulus (G') with double strain amplitude for Nitrol-treated compounds containing 40–60 p.p.h.r. HAF black. Untreated control Compounds 1 and 3 and the NR gum compounds with and without Nitrol treatment are shown for comparison.

faster or longer running of vehicles at speed or under heavy load. In electrically driven vehicles where rolling resistance of the tyre is of prime importance, improved resilience should lead to longer range, more economical operations.

ACKNOWLEDGEMENT

The authors wish to thank the Monsanto Chemical Company for supplying the Nitrol used in this study, and to acknowledge the assistance of Mr. R.E. Whittaker and Mrs. A. Chapman in obtaining and analysing the experimental measurements and Mr. Hon Kok Kee for help during mix preparation. This work forms part of the programme of research of the Natural Rubber Producers' Research Association.

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DISCUSSION

Chairman: Mr. N.P. Bekema

Mr. A.D.T. Gorton asked whether the effect of Nitrol was entirely due to improved dispersion of carbon black by inhibition of breakdown of the compound in the Banbury. Mr. Swift replied that, since Nitrol was not added until the second cycle, it could have no effect during pre-mastication in the first cycle. There was an increase in viscosity probably due more to temporary cross-linking in the unfilled compounds than to inhibition of breakdown.

Mr. I.K. Yeo asked if the three-stage process with overnight storage between stages was practical in a factory with limitations of machinery and storage space. Mr. Swift agreed that such factors, including the introduction of a separate mixing cycle for Nitrol treatment, imposed certain disadvantages; the process was hence likely to be restricted to specialist products. Mr. J. Payne commented that Monsanto had found Nitrol not to be so effective in a single pass Banbury cycle when small laboratory equipment was used; however, when a large Banbury was used, a single pass gave results comparable with two passes. The increased Mooney viscosity was ascribed to weak links through free radicals which broke down on milling. This had been demonstrated in gum stocks. Whether or not this was also the case in black stocks remained undetermined, owing to masking by the black.

Dr. A.A. Watson asked in which natural rubber applications Nitrol was now used. Mr. Swift said this type of promoter had been used mainly in very large tyres. Mr. J. Payne added that the worldwide usage of Nitrol in truck tyres was largely in NR or NR blends, but such promoters had for long been used in butyl rubbers to obtain specific processing and vulcanisate properties.